# EXPERIMENTAL AND NUMERICAL STUDIES OF TRICHLOROETHYLENE MIGRATION

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## 1 INTRODUCTION

Chlorinated solvents represent one category of the most widespread pollutants in soils and aquifers. Among them, the Tricholoroethylene (TCE) is a DNAPL [Pankow and Cherry, 1996]. Its industrial use as a dry cleaner leads to contaminate plenty of industrial sites and justifies a specific study on its behaviour. In porous media, TCE can be found under different forms: pure, volatile and dissolved in water and adsorbed on the solid matrix. Each form is a risk of pollution for soils and aquifers, at long and short terms. In order to focus our study on the phenomena of volatilisation and dissolution, we will not take into account the adsorbed form of the pollutant. In fact, we try to understand and explain the behaviour of TCE in a soil, in order to determine and apply the most appropriate remediation technique for a contaminated site.
The migration of a pollutant through a porous medium is controlled by its physical and chemical parameters but also by the characteristics of the porous medium. For example, these characteristics can be the capillary pressure, hydraulic conductivity, effective porosity ... Moreover, the behaviour of TCE can be different whether it is in the unsaturated zone (at irreducible water saturation) where itc an volatilise in contact with gas phase or in the saturated zone, where it can dissolve in water.
Several studies realised since 1980 [Abriola, 1989; Miller *et al.*, 1990; Powers *et al.*, 1991; Powers *et al.*, 1992; Geller and Hunt, 1993 and Powers *et al.*,19 94]ha ve been interested in mass transfer during dissolution. Other authors [Sleep and Sykes, 1989; Griffol and Cohen, 1996; Cho *et al.*, 1993; Jellali *et al.*, 2001] have focused on the volatilisation of NAPL and especially on vapourm ovements and on the influence of a water infiltration on their dissolution. This study tries to understand and measure the process ofv olatilisation and dissolution ofa DNAPL injected in a homogeneous porous medium.
The aims oft his study are:

*(i)* to dimension, using the numerical results, a 2D experimental set-up allowing to follow the migration ofT CE in a variably water saturated sand,
*(ii)* to compare the experimental and numerical results obtained during an injection of TCE.

## 2 MATERIAL AND METHODS

### 2.1 Simulations with SIMUSCOPP

SIMUSCOPP is a numerical modelling software package developed by the Petroleum French Institute (IFP). It permits to determine the fluid velocities, pressures and concentrations of chemical species in multiphase flow by solving a set of coupled flow and transport equations (Tardy et al., 1996). The chemical species can be found in one, two or three fluid phases. The mass transfer between chemical species can be taken into account or not. In our study, the chemical species is represented by the trichloroethylene (TCE).
In a first time, the numerical code was used in order to determine the optimal dimensions of a laboratory model represented by a column. Then, it was used in order to simulate an experiment

involving the injection, in the upper part of the experimental set-up, of 400 ml of TCE for2 hours. The change of the concentration of vapours and dissolved TCE are followed for one day. The comparison between numerical and experimental data is presented in the last section.

### 2.2 Experimentalse t-up

The experimental set-up (figure 1) is represented by a glass column. Its optimal dimensions, chosen according to numerical simulations, are: 0.2m in diameter and 1.0m inl ength. The columni s progressively filled with water (each time 6 cm of water are maintained above the ground surface) and sand is added by 800 g fractions. The column is struck several times with a hammer to allow the optimisation of grain sand distribution and to avoid compressive effects between each sand level. Once the column is completely filled with water and sand, it is drained by its base. The drainage is stopped when water level is about 0.2 m. So, the saturated zone is located between 0.0 and 0.2 m, the capillary fringe between 0.2 m and 0.5 m approximately and finally, the unsaturated zone between 0.5 m and 1.0 m. We note that the main characteristics of the sand, *i.e.*, hydraulic conductivity, effective porosity, capillary pressure and relative permeability were experimentally determined. These experiments are presented in the third part oft he paper.

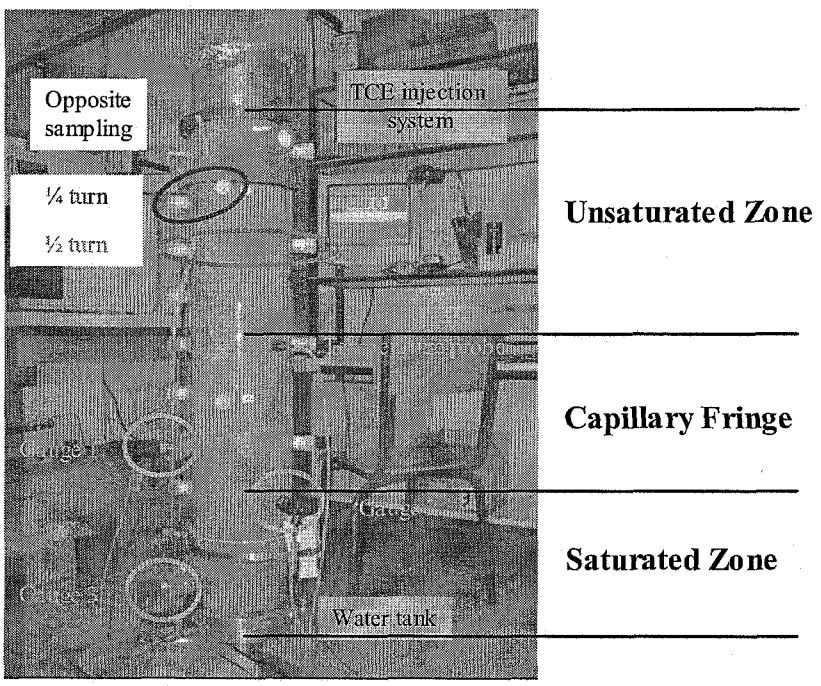


**Figure 1: Experimentalse t-up of TCE injection.**

The column is equipped with 3 pressure gauges and 1 temperature probe. In ordert o allow sampling of gas and water with syringes, 18 holes are located on the column's side. The syringe dimensions permitted sampling at 5.0 cm inside the sand. The samples, mixed with 1 mL of Methanol, which reacts as a trap for pure, volatile and dissolved TCE, are analysed by a gas chromatograph equipped with a flame ionisation detector (FID) and a capillary column. The gases used in the chromatograph are $H_2$, $N_2$ and air. The flow rate of $N_2$ inside the capillary column is about 5 mL/min and its temperature is constant and fixed at 70° C. The temperatures of FID and injector are respectively 250 and 200° C.

## 3 CHARACTERISATION OF THE POROUS MEDIUM

One sand has been used in our experiments. It is coming from a river located in eastern France. Mainly composed of quartz, the properties of this sand are presented in Table 1.

**Table 1: Main characteristics of the sand.**

| Property | Value |
|---|---|
| Mean grain diameter (mm) | 0.56 |
| Minimal density (g/cm3) | 1.43 |
| Maximald ensity (g/cm3) | 1.63 |
| Grain density (g/cm3) | 2.635 |
| Hydraulic conductivity(m/s) | 1.50E-04 |

The capillary pressure - water saturation or retention curve is one of the most significant data for SIMUSCOPP package. Consequently, it has been determined using an experimental device (Figure 2). Represented by a column of dimensions: 0.55 m in length and 0.09 m in diameter, this device is made up of a stack of 8 plexiglas cylinders (9.0 cm in diameter and 7.0 cm in height). The column is completely filled with water and the sand isad ded by fractionso f 400 g. The optimal grain sand distribution is obtained in the same way as for the experimental set-up. Once the column is completely filled with water and sand, iti s drained by its base until the imposed water level is reached.

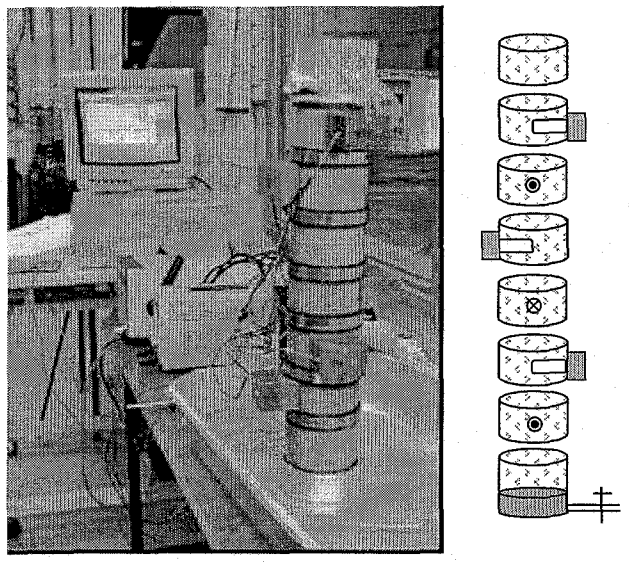

**Figure 2: Experimental set-up for determination of retention curve.**

In order to measure the pressure evolution in the porous medium, a tensiometer probe is attached to each cylinder. One of its end isbu ried into the porousm edium and the other one isli nked to a pressure gauge. At the end of the experiment, the sand is sampled and water saturation is measured. Consequently, for each level corresponding to tensiometerp robes, the stabilised recorded pressure in relation to water saturation can be graphically represented (Figure 3). Six experimentsha ve been carried outan d all experimental points are plotted on Figure 3.
The interpretation of this figure permits to obtain Van Genuchten model parameters, *i.e.*, $\alpha$ and n [Van Genuchten, 1980] that are listed in table 2.

**Table 2: Van Genuchten parameters for the sand.**

| m | n | $\alpha$ [$m^{-1}$] |
|---|---|---|
| 0.70 | 3.36 | 0.084 |

They enable to estimate the relative permeabilities for each two-phase fluid couple in a three-phase system [Van Genuchten,19 80;P arker *eta l.*, 1987].
These experimental and analytical data have been implemented in SIMUSCOPP.

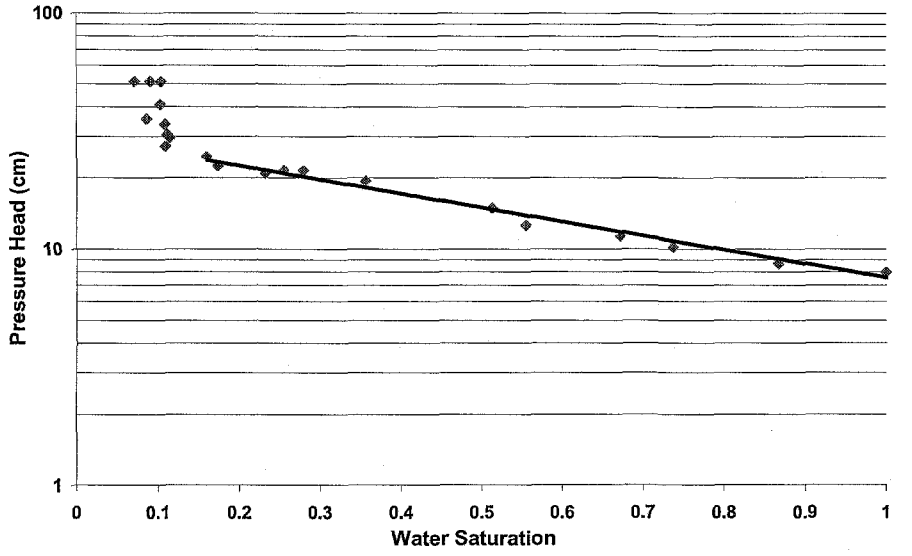


**Figure 3: Retention curve for the sand.**

## 4 COMPARISON OF NUMERICAL AND EXPERIMENTAL RESULTS

The experimental data are numerically analysed using SIMUSCOPP package. The simulated domain, similar to the experimental set-up, is divided into 400 bilinear regular elements of dimensions: 0.005 m in X direction (radius) and 0.01 m in Z direction (length). As in experimental data, 400 ml of TCE are injected for2 hours. The pollutant injection is realised below the upper limit of the domain into an area of 1.5 $cm^2$ corresponding to 3 elementsi n X direction and one element in Z direction. The TCE migration is followed for one day. The comparison between the experimental and numerical results is presented by a spatial and temporal concentration evolution ofv apours and dissolved TCE.

### 4.1 Evolution of TCE vapours

Indicated times on the figures correspond, as far as the experiment is concerned, at the time of the first sample taken of a sampling series. For the simulation it is linked to the state of the model at this specific time. It takes approximately halfan hour to sample an entire series.
On these graphs, the squares represent the mean value of at least 4 experimental values. These experiments have been conducted according to the same procedure. One uncertainty, due to sampling and analyse, is associated with one experiment. The envelope curves around the mean experimental value result from the mean of the overvaluation (or the undervaluation) of each experimental value by its uncertainty. It gives yellow triangles for the high trend and blue triangles for the low trend.
Lozengesr epresent numerical results. The blue ones are related to the simulation that takes into account the sand properties: especially the hydraulic conductivity of about 15 $10^{-4}$ m/s. The red lozenges correspond to a simulation realised with a hydraulic conductivity of 75 $10^{-4}$ m/s. These hydraulic conductivities are respectively assimilated to the intrinsic permeabilities: 15 Darcy and 75 Darcy.

Wec an notice (Figure 4) the increasing evolution of the concentration of TCE vapours, for the experiment as well as fort he simulations, in the column with time. This evolution of vapours is related to the migration ofpu re TCE in the column.
The evolutions of vapours concentration, given by the simulations, are different at the beginning. The blue curve that corresponds to the simulation with the intrinsic permeability experimentally determined presents a slower progression compared with the other and with experiments. On the otherha nd, the red curve that has been realised with anotheri ntrinsic permeability (75 Darcy), has an evolution faster and closer to experimental results.
Moreover, for simulations, once the maximal concentration of TCE vapours is reached, the unsaturated zone of the column is completely saturated by vapours. After 3 hours, one can notice the

decreasing of vapours concentrations in the upper part of the column. This phenomenon reproduces the experimental trend that can be seen at each time, for the upper level.
Although the numerical results are quickly stabilised in the column, this equilibrium state is not so evident for the experimental ones.

### 4.2 Evolution of dissolved TCE

Another graphic representation has been adopted to illustrate the evolution of dissolved TCE in the water of the column. For three levels situated at z= 35, 25 and 15 cm from the base of the column the evolution of dissolved TCE concentration isf ollowed versust ime. Asf or as the evolution of TCE vapours, blue circles correspond to the mean of 4 to 6 experimental results. Two trends are defined considering the mean of the addition or the removal of the uncertainty related to each experiment (yellow and blue triangles).
The numerical results are represented with lozenges: blue ones for the simulation with an intrinsic permeability of15 Darcy and red ones for the simulation with intrinsic permeability of75 Darcy.

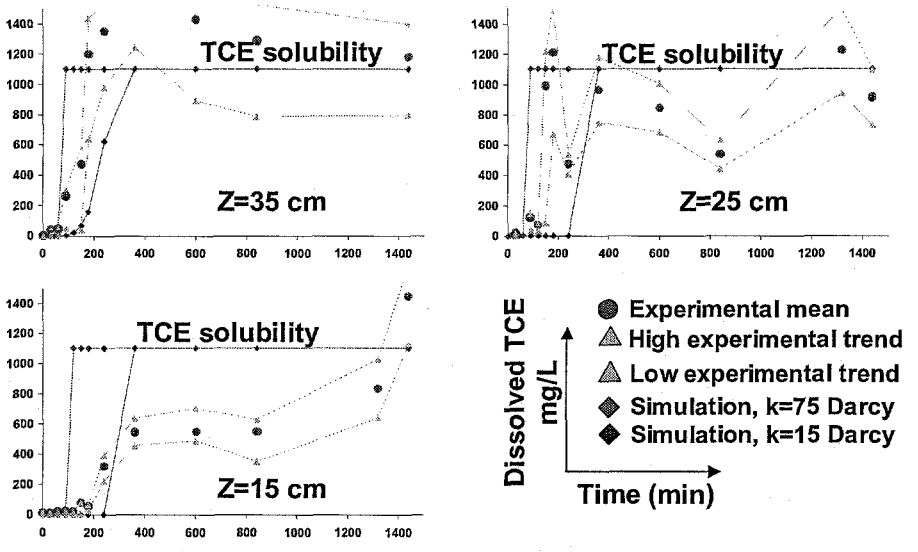


**Figure 4: Calculated and experimentale volution of dissolved TCE concentration.**

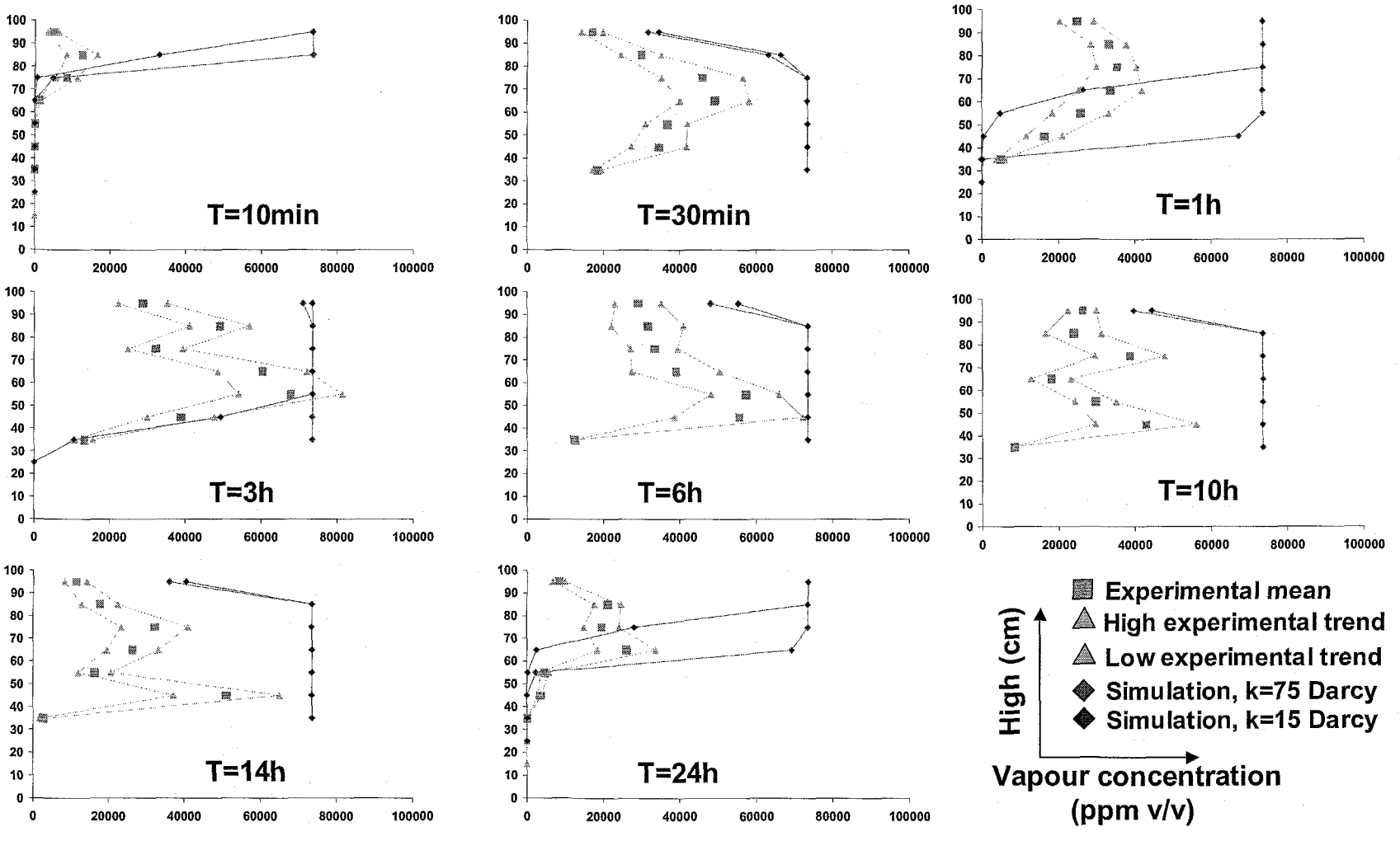


Figure 5: Calculated and experimental evolution of TCE vapours concentration.

For each level, the concentration of dissolved TCE in the water of the column increases with time. The maximum concentration reached corresponds to the solubility ofT CE.
For the experiment, at level z=35 cm, this value is quickly reached (3 hours) and even exceeded it. This is due to the fact that during water sampling, some TCE can be taken with water in the syringe and be analysed. For the other levels, concentrations evolve more slowly. For level z=15 cm, the maximum concentration is reached after 14 hours.
The numerical results are different in the first time of the simulation. The simulation with a higher intrinsic permeability reaches the maximum concentration faster (less than 2 hours), for each level. For the other (intrinsic permeability of 15 Darcy), it takes more time (6 hours) to be completely saturated.
And one can notice that the experimental increase of concentration for each level is between the two simulations.

### 4.3 Discussion

The fact that an equilibrium state is not reached for the vapours and that concentrations in vapours decrease in the upperpa rt of the column may be explained by losses of vapours into the atmosphere. Anothere xplanation can be the evolution (increasing and decreasing of 1° C) of the temperature in the laboratory. Indeed, the physico-chemical properties of the TCE and especially the tension vapour pressure, are very reactive according to temperature. A slight modification of temperature may lead to an increase or decrease of the maximum vapour concentration and may also explain the decreasing of concentration between 4 to 14 hours and the increasing trend around 24 hours.

The experimental evolution of TCE vapours as well as dissolved TCE follows the same trend as the numerical results. However, the simulation with an intrinsic permeability of 75 Darcy seems to be closer to these experimental evolutions (especially for the vapours) than the other simulation, whose data correspond to the experiments. This may be explained, as it was evocated by Pankow and Cherry [1996], by the fact that the hydraulic conductivity is experimentally determined for water in a water saturated porous medium and not according to the physical properties of the TCE (density and dynamic viscosity). These properties may increase the TCE speed migration in the porous medium. That can be a reason why the simulation with a higher intrinsic permeability fits better experimental results than the other one.

## 5 CONCLUSION

This study presents an experimental device devoted to the study of the migration of a DNAPL in a homogeneous porous medium. This set-up allows to follow the volatilisation and dissolution of TCE in the air or water of the column. These phenomena can be numerically reproduced with SIMUSCOPP. The evolutions of the experimental and numerical results for each phase are similar. But, the simulation that seems to fit better the experimental results, takes into account a higher intrinsic permeability than the experimental value. That brings into relief the fact that the assimilation of the hydraulic conductivity with the intrinsic permeability for a porous medium may be used carefully by taking into account the differentf luids involved.
Another noticing results are the development of a sampling procedure for different form of TCE and their analyses by gas chromatography. The method that has been adjusted for these experiments allows to: *(i)* trap vapours of TCE and dissolved TCE in a same solvent (methanol) and *(ii)* determine the level ofc oncentration of TCE in each phase.
This experimental device and the analytical procedure will be used with different porous media and pollutants. After those studies, heterogeneities might be introduced. Another application of this experimental set-up may be the test of different techniques of remediation (injection of surfactant in the medium,i njection ofa ir...).
The numerical code is already used at the site scale in order to evaluate the migration of a pollutant and dimension remediation techniques.

## 6 REFERENCES


ABRIOLA L.M. - Modeling multiphase migration of organic chemicals in groundwater systems. A review and assessment. Environmental Health Perspectives,v ol 83, p117-143, 1989.

CHO H.J., JAFFE P.R. and SMITH J.A. - Simulating the volatilisation of solvents in unsaturated soils during laboratory and field infiltration experiments. Water Resources Research, vol 29, N° 10, p 3329-3342, 1993.

GELLER J.T. and HUNT J.R. – Mass transfer from non-aqueous phase organic liquids in water-saturated porous media. Water Resources Research,v ol 29, N° 4,p 83 3-845, 1993.

GRIFFOL J. and COHEN Y. – Contaminant migration in the unsaturated soil zone: the effect of rainfall and evapotranspiration. Journal ofC ontaminant Hydrology, vol 23, p 185-211, 1996.

JELLALI S., MUNTZER P, RAZAKARISOA O. and SCHÄFER G. – Large scale experiment on transport of Trichloroethylene in a controlled aquifer. Transport in Porous Media. Vol 44, p 145-163, 2001.

MILLER C.T., POIRIER-McNEIL M.M. and MAYER A.S. – Dissolution of trapped non-aqueous phase liquids : mass transfer characteristics. Water Resources Research, vol 26,N ° 11,p 27 83-2796, 1990.

PANKOW J.F. and CHERRY J.A. – Dense chlorinated solvents and other DNAPLs in groundwater: History, Behavior,an d Remediation.W aterloo Press, Ontario,C anada, 260 p,19 96.

PARKER J.C., LENHARD R.J. and KUPPUSAMY T. – A parametric model for constitutive properties governing multiphase flow in porous media. Water Resources Research, Vol 23, N° 4, p 618 – 624, 1987.

POWERS S.E., LOUREIRO C.O.,AB RIOLA L.M. and WEBER W.J. – Theoretical study of the significance of non-equilibrium dissolution of non-aqueous phase liquids in subsurface systems. Water Resources Research, vol 27,N ° 4, p 463-477,19 91.

POWERS S.E., ABRIOLA L.M and WEBER W.J. – An experimental investigation of non-aqueous phase liquid dissolution in saturated subsurface systems : steady state mass transfer rates. Water Resources Research, vol. 28, N° 10, p 2691-2705, 1992.

POWERS S.E., ABRIOLA L.M and WEBER W.J. – An experimental investigation of non-aqueous phase liquid dissolution in saturated subsurface systems : transient mass transfer rates. Water Resources Research, vol. 30, N° 2,p 32 1-332, 1994.

SLEEP B.E. and SYKES J.F. – Modelling the transport of volatile organics in variably saturated media. Water Resources Research,v ol 25, N° 1,p 81-92,19 89.

TARDY P., QUINTARD M., LE THIEZ P. and SEVA E. – A numerical model of hydrocarbon contaminant flow in soil and aquifers. Development and Application of Computer Techniques to Environmental Studies VI. Ed P. ZANNETTI and C.A. BREBIA, Computational Mechanics Publications, Southampton, 1996.

VAN GENUCHTEN M. Th. – A closed-form equation for predicting the hydraulic conductivity of unsaturated soils.S oil Sci. Soc. Am. J., vol 44,p 89 2 – 898,1980.